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Measurements of ultrafine particles carrying different number of charges in on- and near-freeway environments

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HIGHLIGHTS

► Electrical charges on ultrafine particles (UFPs) were measured on- and near-freeways.
► The fractions of charged UFPs were significantly higher on the freeways than in the background.
► Charged particles decayed faster than total particles but slower than ion downwind from the freeway.
► Strong net positive charges were found on nucleation mode particles near freeways.

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ABSTRACT

This paper presents measurements of electrical charges on ultrafine particles (UFPs) of different electrical mobility diameters (30, 50, 80, and 100 nm) in on- and near-freeway environments. Using a tandem Differential Mobility Analyzer (DMA) system, we first examined the fraction of UFPs carrying different number of charges on two distinctive freeways: a gasoline-vehicle dominated freeway (I-405) and a heavy-duty diesel truck dominated freeway (I-710). The fractions of UFPs of a given size carrying one or more charges were significantly higher on the freeways than in the background. The background UFPs only carried up to two charges but freeway UFPs could have up to three charges. The total fraction of charged particles was higher on the I-710 than I-405 across the studied electrical mobility diameters. Near the I-405 freeway, we observed a strong decay of charged particles on the downwind side of the freeway. We also found fractional decay of the charged particles was faster than total particle number concentrations, but slower than total ion concentrations downwind from the freeway I-405. Among charged particles, the highest decay rate was observed for particles carrying three charges. Near the I-710 freeway, we found strong net positive charges on nucleation mode particles, suggesting that UFPs were not at steady-state charge equilibrium near freeways.

1. Introduction

Traffic emissions usually constitute the largest source of ultrafine particles (UFPs, $D_P < 100$ nm) in an urban environment (Shi et al., 2003). Several studies have found that the combustion process in the engine generated ion concentrations in the range of 10^8–10^{11} cm^{-3} (Fialkov, 1997; Yu et al., 2004). Nucleation mode UFP formation occurs in the presence of high ion concentrations (Yu, 2001). Once generated, the ion concentration drops rapidly with increasing distance from the source as a result of dissipation through either ion–ion recombination or ion-particle attachment (Arnold et al., 2000). In the process of ion-particle collisions, UFPs take different number of positive or negative charges (n charges).

The presence of the charges on particles may substantially affect coagulation and particle transport mechanisms. Leppa et al. (2011) have shown that charged particles enhanced the coagulation process. They found that particles carrying n charges increased coagulation-driven particle growth rate by a factor of 1.5–2 and resulted in a decreased particle number concentration. The enhanced coagulation not only makes particle grow in size but also changes agglomerate geometry, and thus modifies particle diffusion coefficients (Jacobson and Seinfeld, 2004). Subsequently, the change in diffusion

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coefficient affects particle transport behaviors. For example, electric charges on smaller UFPs were found to contribute to a lower penetration factor across idealized vehicle cracks (Xu et al., 2010).

Besides coagulation and penetration, the electric charges on particles are also important to understand particles scavenged by the atmospheric water droplets. In comparison to neutral particles, the charged particles have about an order of magnitude higher scavenging coefficients than the neutral particles at a diameter of 100 nm; whereas, the scavenging coefficients of charged particles become comparable to those of neutral particles at diameters less than 10 nm (Andronache, 2004). Thereby scavenging effects is more important in the size range of the Greenfield gap (i.e., 10 nm $< D_p <$ 2 μm) (Tinsley et al., 2000). Scavenging coefficients are found approximately two orders of magnitude higher for 1-nm particles than for 100-nm particles (Andronache, 2004). Since the changes in scavenging coefficient occur from the electrical image force of charged particles, scavenging effects are independent from the charges of the water droplets (Tripathi and Harrison, 2002).

Charged particles have been previously observed in combustion processes. Kim et al. (2005) has used a tandem Differential Mobility Analyzer (DMA) system to study charged particle distributions in a lab-scale combustion system with ethylene gas as the fuel. The fraction of charged particles from gasoline and diesel engine exhausts has also been studied with a similar tandem DMA system (Maricq, 2006). Both studies found agreement between the measurements and charge equilibrium theory at high temperature (i.e., 800–1300 K). However, these results may not be directly applicable to charged particles at ambient temperature on and near-roadways since the charge equilibrium theories are a strong function of the temperature.

Previous studies have also reported high concentrations of UFPs in the on- and near-roadway atmosphere with sharp concentration decay downwind from the freeways (Zhu et al., 2002a, 2002b). A recent study found that cluster ion concentrations have even greater decay rates as a function of distance away from a freeway than UFP number concentrations (Jayaratne et al., 2010). An ion concentration in the range of 400–600 cm^{-3} has been reported in the near-roadway atmospheres (Ling et al., 2010).

No study, to the best of our knowledge, has experimentally quantified the fraction of UFPs carrying *n* charges on and at increasing distances downwind from roadways. This knowledge gap limits our understanding of particle dynamics (e.g., coagulation, transport, transformation, and scavenging) in the on- and near-roadway atmospheres. In this paper, we report the fraction of charged particles observed on and near two major Los Angeles freeways (i.e., I-405 and I-710) and discuss the effects of charge polarity with respect to particle size and number of charges.

2. Methodology

2.1. Instrumentation

2.1.1. Tandem DMA configurations

A tandem DMA system with two differential mobility analyzers (DMA, Model 3080, TSI Inc., St. Paul, MN) in series was used in this study. Fig. 1 illustrates the schematic experimental setup of the tandem DMA system configuration. The selector DMA allows UFPs of a certain electrical mobility to go through. While maintaining the same particle electrical mobility, particles carrying both single and multiple charges pass through the selector DMA. Since the electrical mobility is a function of both number of charges and particle diameter (See Eq. (1)), particles carrying different number of charges have different sizes accordingly. For example, doubly charged particles have a diameter larger than singly charged particles. Similarly, the diameter of particles carrying triple charges is always larger than that of particles carrying double charges.

Particles from the selector DMA are then classified by the number of charges in the following SMPS system – a combination of an electrostatic classifier (Model 3080, TSI Inc., St. Paul, MN), a second DMA (Model 3081, TSI Inc., St. Paul, MN), and a condensation particle counter (Model 3785, TSI Inc., St. Paul, MN). The selected particles first pass through a Kr^{85} neutralizer (Model 3077A, TSI Inc., St. Paul, MN) to redistribute the charges on the particles, whereby most of the multiply charged particles are brought to Boltzmann equilibrium charge distributions with less than 10% remained in multiple charge states (Wiedensohler and Fissan, 1991). The second DMA classifies the particles in 102 channels of particles diameter. Consequently, the tandem DMA system presents particle size distributions with multiple modes. Each mode corresponds to the size of the charged particles carrying different number of charges. The primary mode indicates singly charged particles. Particles having double- and triple-charges can be found at secondary and tertiary modes, respectively. Therefore, number concentration of particles with different number of charges can be determined from the spectra of the tandem DMA system.

2.1.2. Instrument set-up

In this study, the selector DMA was set to sample UFPs of four different electrical mobility diameters (i.e., 30, 50, 80, and 100 nm) representing the typical particle size range observed on- and near-freeways. Scanning in the range of 7–289 nm, the SMPS system characterizes the number concentrations of the charged particles. The experiments were conducted for particles having both positive and negative charges. It should be noted that only particles carrying positive charges were detected with the default electrostatic classifier setup. To measure the concentration of particles with negative charges, the polarity of the high voltage applied to the center DMA rod was reversed by installing a positive high voltage power supply unit (Model 10A12-P4-M, TSI Inc., St. Paul, MN).

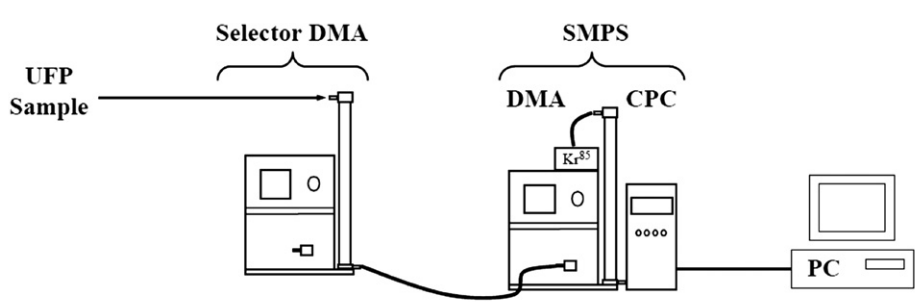

Fig. 1. A schematic of the experimental setup: the tandem Differential Mobility Analyzer (DMA) system includes a selector DMA and a Scanning Mobility Particle Sizer (SMPS). The Kr^{85} charge neutralizer was installed only on the SMPS system.

2.2. Experimental

Using the same instrumental set-up described above, the measurements were repeated in on- and near-freeway environments.

2.2.1. On-freeway environment

A vehicle equipped with the aforementioned tandem DMA system was employed for on-freeway experiments. During on-freeway measurements, a sampling inlet was placed outside the vehicles to bring on-freeway UFPs into the instruments when driving in the middle lane. Since different engine types and loadings lead to different ion concentrations (Yu et al., 2004), two distinguishable freeways were selected to represent different traffic environments: 1) a gasoline-vehicle dominated freeway (I-405 with less than 5% of heavy-duty diesel truck traffic) and 2) a diesel-truck dominated freeway (I-710 with approximately 20%

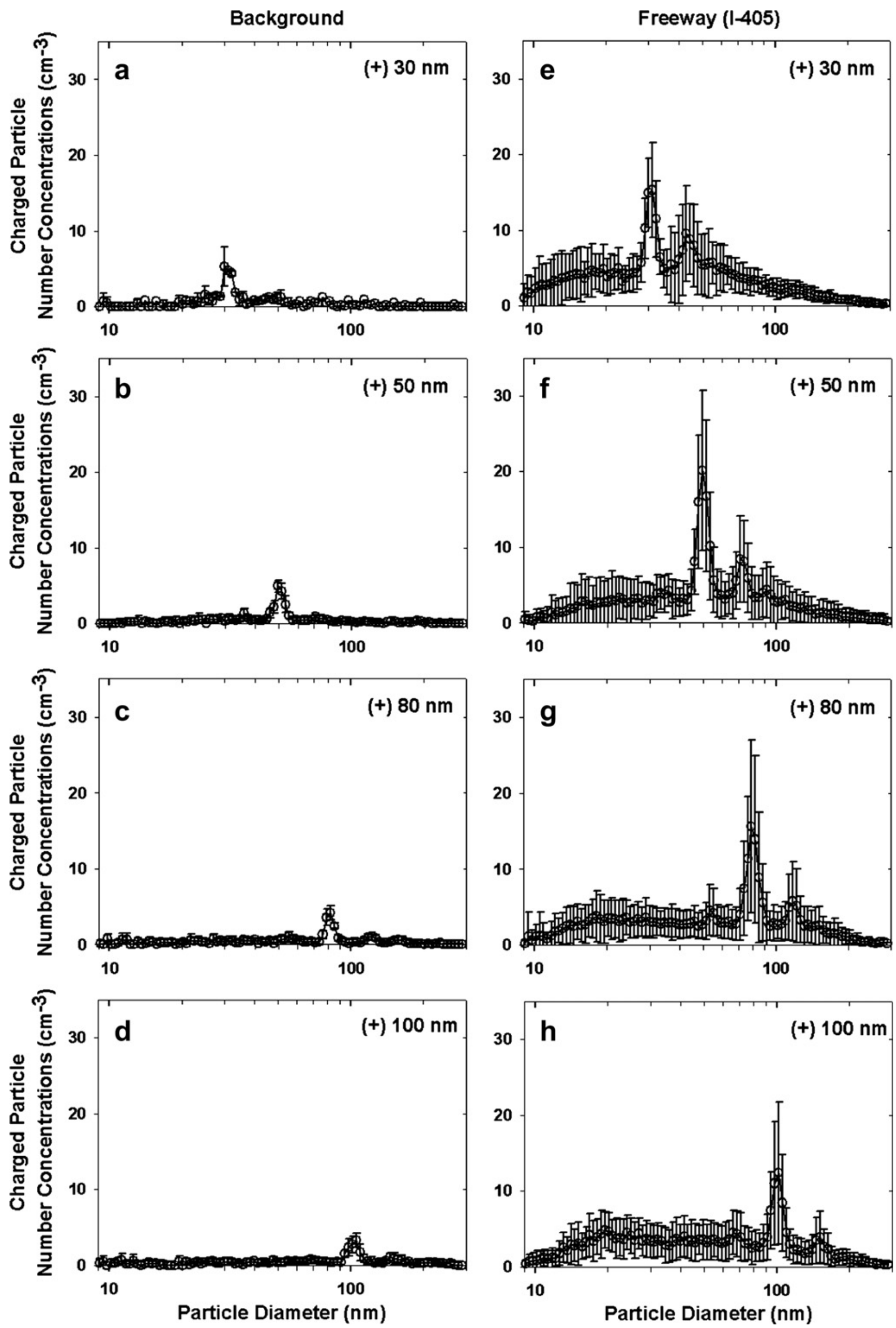

Fig. 2. Size distributions of positively charged particles are presented at different electrical mobility diameters: 30 nm (panels a, e), 50 nm (panels b, f), 80 nm (panels c, g), and 100 nm (panels d, h) in the background (panels a–d) and on the I-405 freeway (I-405, panels e–h). The circle symbols and the error bars are the average and one standard deviation of the observations.

of heavy-duty diesel truck traffic). While I-405 is widely used as a commuting route, I-710 is a major truck route in Southern California. Because diurnal traffic volume changes have regular patterns during weekdays, to minimize the effects of varying traffic volume, measurements were conducted in the afternoon (from 2 to 6 pm) on six different weekdays: four days (i.e., 3/3, 3/29, 4/13, and 4/25 in 2011) on the I-405 and two days (i.e., 12/14/2010 and 1/28/2011) on the I-710. The same instrument set-up and experimental protocols were applied to the measurements on both freeways.

2.2.2. Near-freeway environment

The near-freeway measurements of charged particles were conducted on Constitution Avenue at the Los Angeles National Cemetery, located on the east side of the I-405 freeway. The selected site was desirable because of its proximity to the freeway and the lack of nearby UFP emission sources other than emissions from the freeway traffic. During the sampling periods, there was a consistent eastward sea breeze (1.78 ± 0.89 m s^{-1}) carrying UFPs emitted on the freeway directly to the sampling locations. Measurements were taken upwind and at 10, 20, 50, and 100 m downwind from the edge of I-405 and repeated in the afternoon (from 12 to 3 pm) on four different days (i.e., 2/22, 3/10, 3/29, and 4/25 in 2011). A detailed description of the study site can be found elsewhere (Zhu et al., 2002b).

charged particles could be found at a tertiary mode diameter: always larger than the secondary mode diameter.

To verify that each mode diameter corresponds to particles carrying n charges but with the same electric mobility, the following particle electrical mobility equation (Willeke and Baron, 1993) was used:

$$Z_P = \frac{neC}{3\pi\mu D_P} \tag{1}$$

$$C = 1 + \frac{2\lambda}{D_P}\left(1.257 + 0.40 \cdot \exp^{-\frac{0.55 \cdot D_P}{\lambda}}\right) \tag{2}$$

where, Z_P is the particle electrical mobility (m^2 s V^{-1}); n is the number of electric charges (−); e is the elementary charge (1.6×10^{-19} C); μ is air viscosity (1.78×10^{-5} kg m^{-1} s^{-1}); D_P is particle diameter (m); C is Cunningham slip correction factor, which can be calculated from Eq. (2); and λ is the air mean free path (6.8×10^{-8} m).

The fractions of particles carrying different charges (e.g., +1, +2, +3, −1, −2, and −3) were then estimated by dividing the charged particle concentrations with the total particle concentrations of each mode.

$$(\text{Fraction of UFPs carrying } n \text{ charges}) = \frac{(\text{Charged particle number concentration at a mode diameter})}{(\text{Particle number concentration at the corresponding mode diameter})} \times 100 \tag{3}$$

2.2.3. Electric charge polarity

To characterize charge polarity, both positively and negatively charged particles were measured near the I-710 freeway in Long Beach, CA. The I-710 freeway generally runs from north to south but the studied section runs 30° to the east. A large flood plain and Los Angeles River are located on the immediate east side of the freeway. There is no significant source of UFPs or any charged particles in the study area other than freeway traffic emissions. In a close proximity to the freeway (15 m from the edge of the 710 freeway), we measured both positive and negative charges on particles of predetermined electrical mobility diameters (i.e., 30, 50, 80, and 100 nm). For each combination of particle size and polarity, data were collected for 24 h continuously. The total experimental period lasted for eight days (11/17 through 11/25 in 2011). Only data collected when the wind direction was about perpendicular to the freeway center-line and at a $300° \pm 45°$ angle were used for freeway emissions. Data collected when the wind direction was about perpendicular to the 710 center-line but at a $120° \pm 45°$ angle were classified as background concentration.

2.3. Analytical

We examined the discrete peaks in SMPS size distribution profiles to determine the fractions of particles carrying different numbers of positive or negative charges. For example, for a selected electrical mobility diameter, the singly charged particles were found at the highest peak of the smallest particle size among all concentration peaks. Particle at this peak representing singly charged particles (i.e., $n = 1$ in Eq. (1)), remained at the electrical mobility diameter preset by the selector DMA. The doubly charged particles were found at a secondary mode that was larger than the primary mode diameter in the size distribution. Similarly, the triply

Depending on the number of charges, the corresponding mode can be primary ($n = 1$), secondary ($n = 2$), and tertiary ($n = 3$). Eq. (3) was then applied to determine the fractions of particles carrying n positive or n negative charges on and near freeways.

3. Results and discussion

3.1. Charged UFPs on freeways

Freeway UFPs of four electric mobility diameters of 30, 50, 80, and 100 nm were investigated. Fig. 2 displays the size spectra of particles with n positive charges in the background (Fig. 2a–d) and

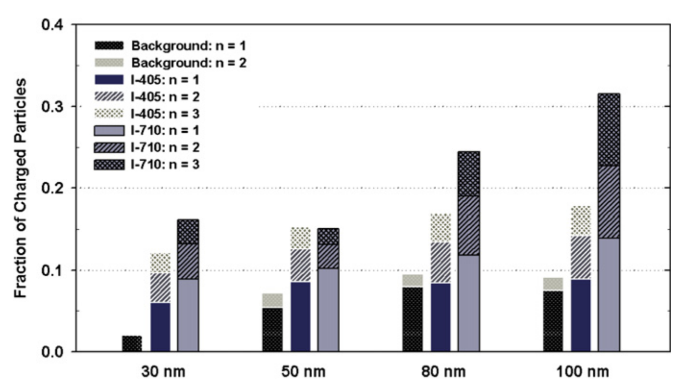

Fig. 3. Average fractions of charged particles measured in the background, and on the freeways I-405 and I-710 with respect to different electrical mobility diameters. Background data were collected near the I-710 freeway under upwind conditions.

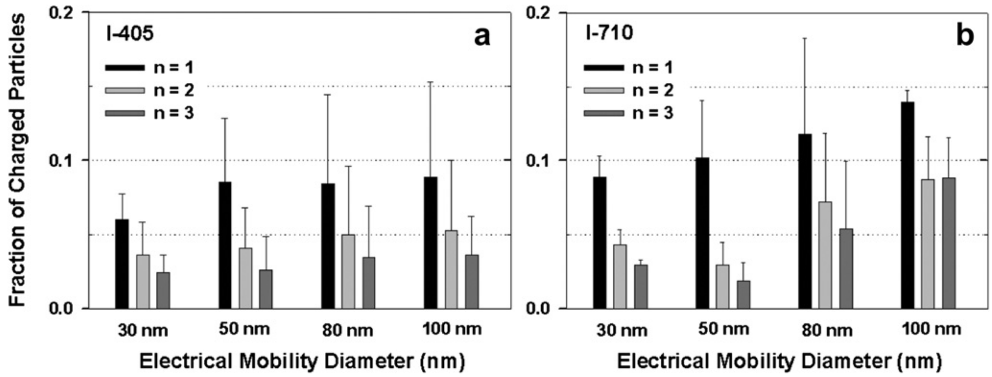

Fig. 4. Fraction of charged particles on (a) the I-405 and (b) the I-710 are plotted by the number of charges (n) at four different electrical mobility diameters: 30, 50, 80, and 100 nm. The error bars represent one standard deviation.

on the I-405 freeway (Fig. 2e–h). Concentrations of charged particles (Fig. 2e–f) were approximately ten-fold higher on the I-405 (Fig. 2a–d), primarily because particle concentrations were much higher on the freeway than in the upwind background. The overall distributions exhibit multi-modes. Primary and secondary modes indicate number concentrations of singly and doubly charged particles, respectively. The diameter (D_P) of the doubly charged particles from the theoretical calculation (Eqs. (1) and (2)) quantitatively matches the experimental measurement shown in Fig. 2. For example, doubly charged particles having an electrical mobility diameter of 30 nm (i.e., $n = 2$ in Eq. (1)) are equivalent to singly charged particles having an electrical mobility diameter of 42 nm, which is close to 43 nm as indicated by the secondary mode in Fig. 2e. Similar results were obtained for other electrical mobility diameters presented in Fig. 2.

UFPs on the freeway can take up to three charges (Fig. 2e–h) whereas the background particles carry only up to two charges (Fig. 2a–d). This is likely because particles emitted from engine combustion processes tend to carry more charges. A previous study reported that UFPs from direct measurements of tailpipe emissions could have up to four charges (Maricq, 2006). Since particles collected on-freeways experienced much longer residence time in the atmosphere than particles directly emitted from the engine exhaust, highly charged ($n = 4$) particles may dissipate immediately in the process of collision with oppositely charged ions or particles before being sampled on the freeway. This may explain why no UFPs with four charges were observed in this study.

Fig. 3 compares the fraction of charged particles in different environments: at the background, and on freeways I-710 and I-405. The fraction of 30 nm particles carrying n charges was the lowest among the four studied electrical mobility diameters. The fraction increases with increasing particle electrical mobility diameter. The highest fractions were commonly found at 100 nm for all comparisons. This observation concurs with Boltzmann charge equilibrium theory in that larger particles would acquire more electric charges due to greater surface areas for ion collisions.

As shown in Fig. 3, the fraction of particles carrying n charges varied substantially under different conditions. In the background, the fraction of particles carrying at least one charge remained less than 10% for the studied electrical mobility diameters. In contrast, a much higher fraction of charged particles (e.g., up to 32% for 100 nm particles) was found on the two freeways. Across all studied

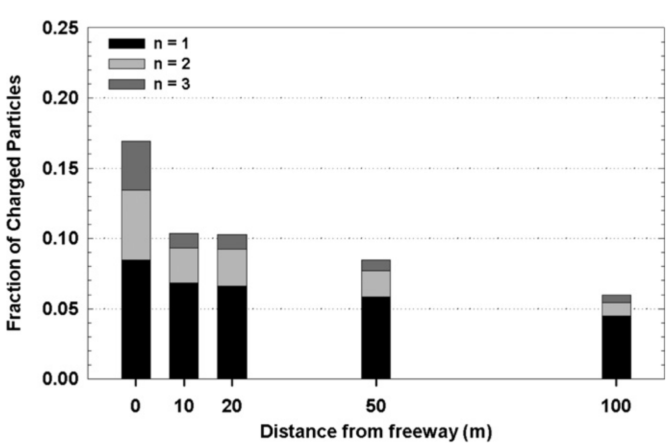

Fig. 5. Fractional changes of charged particles at electrical mobility diameters of 80 nm are presented as a function of downwind distances from the I-405 freeway: 0 m (on the freeway), 10, 20, 50, and 100 m from the edge of the I-405. Different schemes of shade symbolize different number of positive charges (n).

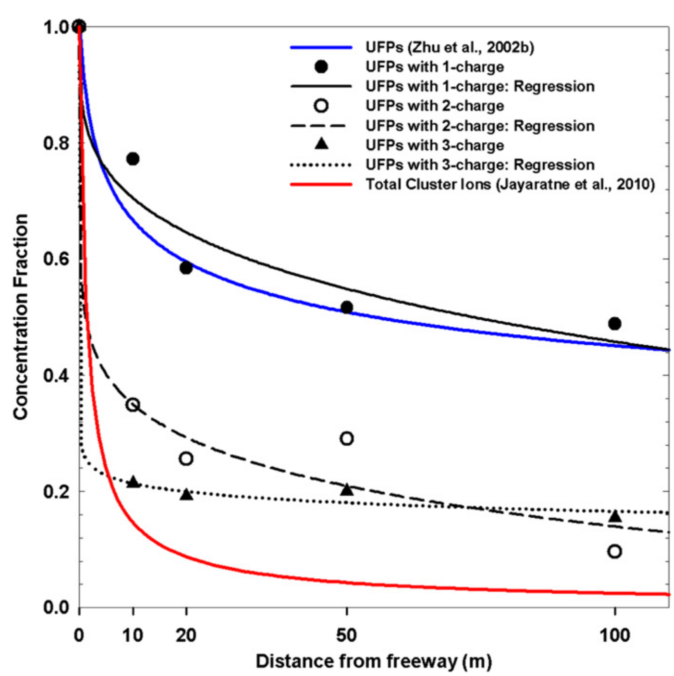

Fig. 6. Normalized concentrations of 80 nm particles carrying n charges as a function of downwind distances from the I-405 freeway. Data were compared to the decay profiles of total particle number concentration (Zhu et al., 2002b) and total cluster ions (Jayaratne et al., 2010) downwind of freeways.

Table 1
A summary of near-freeway pollutant decay functions for ultrafine particles (UFPs) carrying n charges and for total particle number concentration and total cluster ions reported in previous studies.

Measured species near freeways	Number of charges (n)	Regression equations	Determination coefficients (R^2)	Sources
Total particle number concentration	n/a	$y = (x+1)^{-0.18}$	0.84	Zhu et al. (2002b)
UFPs carrying n charges	1	$y = (x+1)^{-0.16}$	0.95	This study
	2	$y = (x+1)^{-0.42}$	0.97	
	3	$y = (x+1)^{-0.51}$	0.97	
Total cluster ions	n/a	$y = (x+1)^{-0.80}$	0.83	Jayaratne et al. (2010)

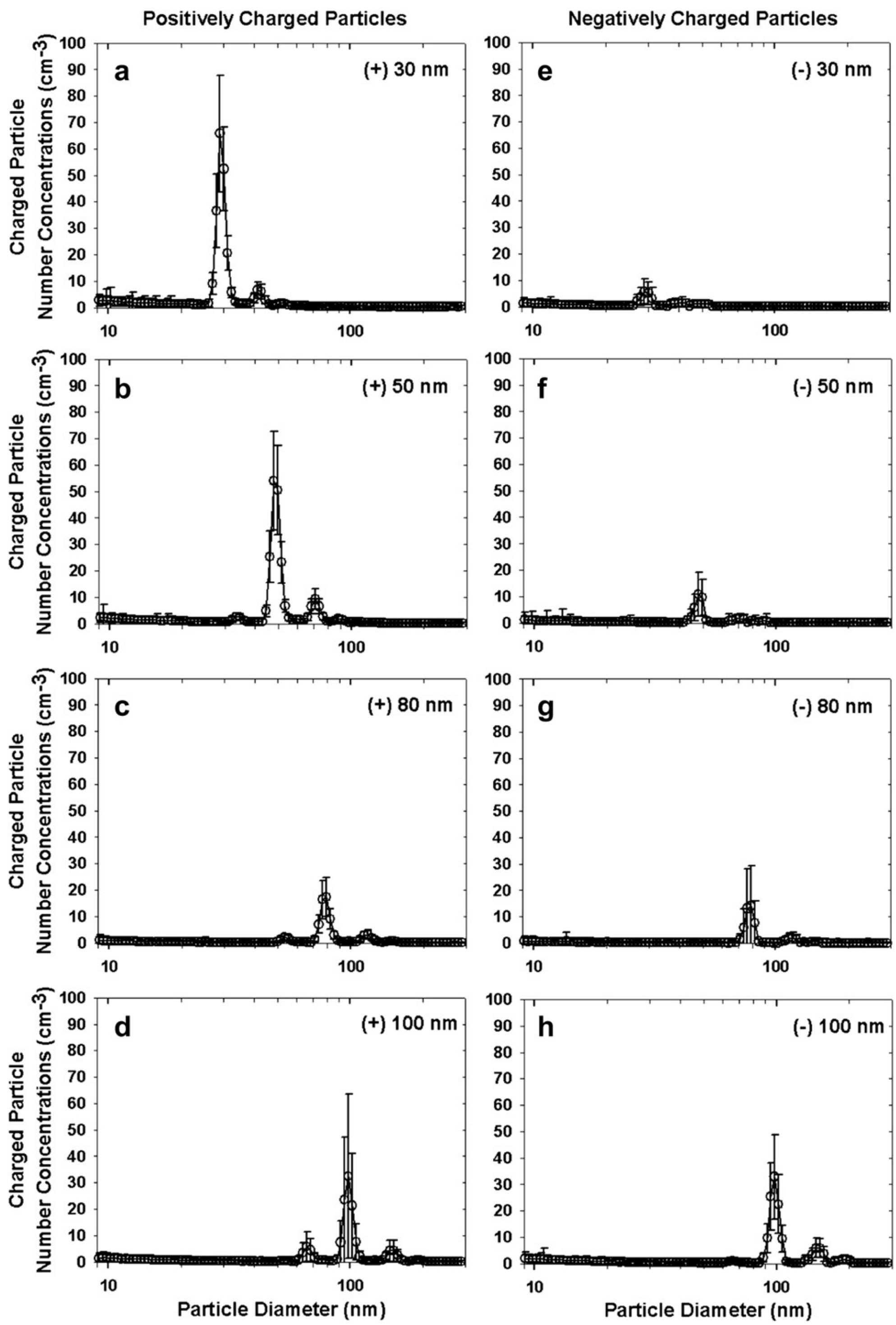

Fig. 7. Positively (panels a–d, on the left) and negatively (panels e–h, on the right) charged particle distributions measured near the I-710 freeway. Data were presented for different combinations of electrical mobility diameters and polarities: ±30, ±50, ±80, and ±100 nm. The circle symbols and the error bars are the average and one standard deviation of the observations.

electrical mobility diameters, the fractions of particles carrying two and three charges were much higher on the freeways than in the background. Specifically, 30 nm particles hardly took more than one charge at the upwind background location. However, higher fractions of particles carrying two or three charges were observed on the freeways. It suggests that motor-vehicle emissions are a strong source contributing to not only UFPs number concentrations but also a high fraction of charged particles in the atmosphere.

The high fraction of charged particles observed on and near freeways will likely increase particle coagulation rates in comparison with the background. As indicated in Leppa et al. (2011), for particles of 1.5–20 nm count median diameter carrying a single charge, the particle growth rate by coagulation could be increased up to a factor of two. The fraction of charged particles reported in this study is within the range of modeling input in Leppa et al. (2011), whereas this study found higher fractions of particles carrying two or three charges. Thus, a factor of greater than two is expected. It should be noted, coagulation is a complicated dynamic process in which particle number concentration and fractal dimension also play important roles. Coagulation rate also changes with time. A full understanding of the impact of particle charge on coagulation rate is beyond the scope of the current work and deserves future research.

Comparing data collected on the two freeways, we found the number concentration of charged particles remained at the same order of magnitude but the fractions were usually higher on the diesel-vehicle dominated I-710 than on the gasoline-vehicle dominated I-405. Fig. 4 further illustrates this point where the fractions of singly charged particles ranged from 0.06 to 0.09 on the I-405 (Fig. 4a) and from 0.09 to 0.14 on the I-710 (Fig. 4b). The differences between the two freeways were relatively small for particles of 30 and 50 nm and even smaller for particles carrying double or triple charges in these size ranges. On the other hand, at 80 and 100 nm, the fractions of charged particles were significantly higher, two times greater for doubly and triply charged particles on I-710 than I-405. Although the fractions of singly charged particles were not as significant as the fractions of particles with double or triple charges, the singly charged particles also showed higher fractions at 80 and 100 nm on I-710 than I-405. Because heavy duty diesel vehicles are a primary source of high ion concentrations on and near a freeway (Jayaratne et al., 2010), the high diesel vehicle traffic was likely causing the high fractions of charged particles on the I-710 freeway.

3.2. Charged UFPs near freeways

Fig. 5 depicts the fraction of charged particles as a function of downwind distances from the I-405 freeway. Overall, the total fraction of all charged particles reduced greatly (i.e., from 0.17 to 0.10) within the first 10 m downwind of the I-405. It then further decayed gradually toward the background level (0.06) at 100 m. In addition, the fractional decay occurred more rapidly for particles with double or triple charges than those with single charge at increasing downwind distances from the I-405. For instance, within 100 m from the freeway, the fractions of singly charged particles reduced by 47% (i.e., from 0.08 to 0.04). However, the fractions of particles with double or triple charges dramatically decrease by 82% (i.e., from 0.05 to 0.01) and 84% (i.e., from 0.03 to 0.01), respectively. The observed decay is likely due to both atmospheric dilution and charge neutralization from particle collision with other ions (or electrons) or to a less extent with other particles carrying opposite charges.

To further investigate the effects of the number of charges on particle concentration decay downwind from freeways, Fig. 6 compares the decay rates of particles carrying different number of charges with previously published data for total particle number concentration and ion concentration near freeways. The downwind concentration was normalized to on-freeway (i.e., 0 m) concentration for particles carrying single, double, and triple charges, respectively. The decay rates of total particle number concentration (Zhu et al., 2002b) and total cluster ions (Jayaratne et al., 2010) were also plotted for comparison. As shown in Fig. 6, in general, the decay rates of charged particles were between total particle (i.e., decay rate of −0.18) and total cluster ions (i.e., decay rate of −0.80) decay curves, with only one exception of singly charged particles (i.e., decay rate of −0.16). Similar to total particle and total cluster ions near freeways, the decay curves of charged particles also stabilized as moving away from the freeway. The decay rates of the charged particles also depended on the number of charges. Particles with triple charges experienced the highest decay rate (−0.51) and followed by those with double charges (−0.42); whereas, particles carrying single charge decreased moderately (i.e., decay rate of −0.16) within the same distance. Table 1 summarizes the regression data of fractional decay functions presented in Fig. 6.

Although particles are a sink for ionic deposition and in return taking on charges, it is a relatively slow process in comparison with ion-electron collision because the mobility of an ion (or electron) is much faster than that of a particle. Ion (or electron) dissipation occurs primarily through bipolar ion-electron collisions so that the fastest decay is found for total cluster ions. The decay of total particle number concentration is primarily a mechanism of [1)] dilution near freeways with minor effects of coagulation by Brownian diffusion. Intrinsically, any charged UFP decay includes the aforementioned two mechanisms: [1)] dilution with minor coagulation by Brownian diffusion and [2)] neutralization by colliding with other ions (or electrons). Moreover, they could also decay via [3)] particle coagulation enhanced by charges on the particle surface. Thus, the downwind decay function of charged particles represented a combined effect of the aforementioned three mechanisms.

3.3. Effects of charge polarities

Fig. 7 shows typical charged particle size distribution for different electrical mobility diameters with different polarities: positive (Fig. 7a–d) and negative (Fig. 7e–h), 15 m from the I-710 freeway. In general, there were more particles with *n* positive than *n* negative charges for studied particle sizes. The differences were more significant for 30 and 50 nm particles (Fig. 7a, b vs. Fig. 7e, f) than 80 and 100 nm particles (Fig. 7c, d vs. Fig. 7g, h). For 30 and

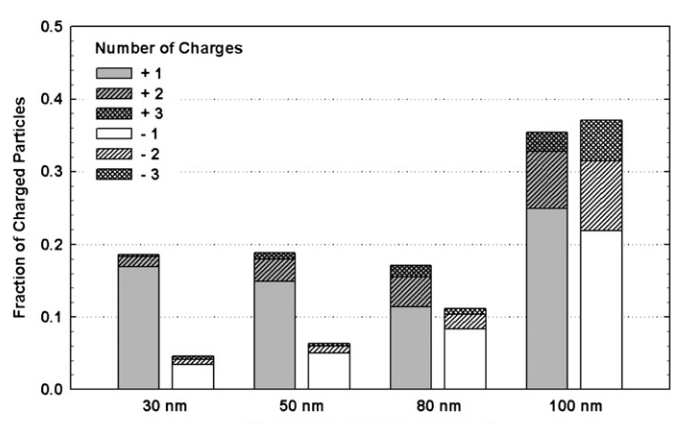

Fig. 8. Fractions of charged particles at four electrical mobility diameters: 30, 50, 80, and 100 nm. The stacked bars represent either positively (gray) or negatively (white) charged particles with different number of charges and polarities (e.g., ±1, ±2, and ±3).

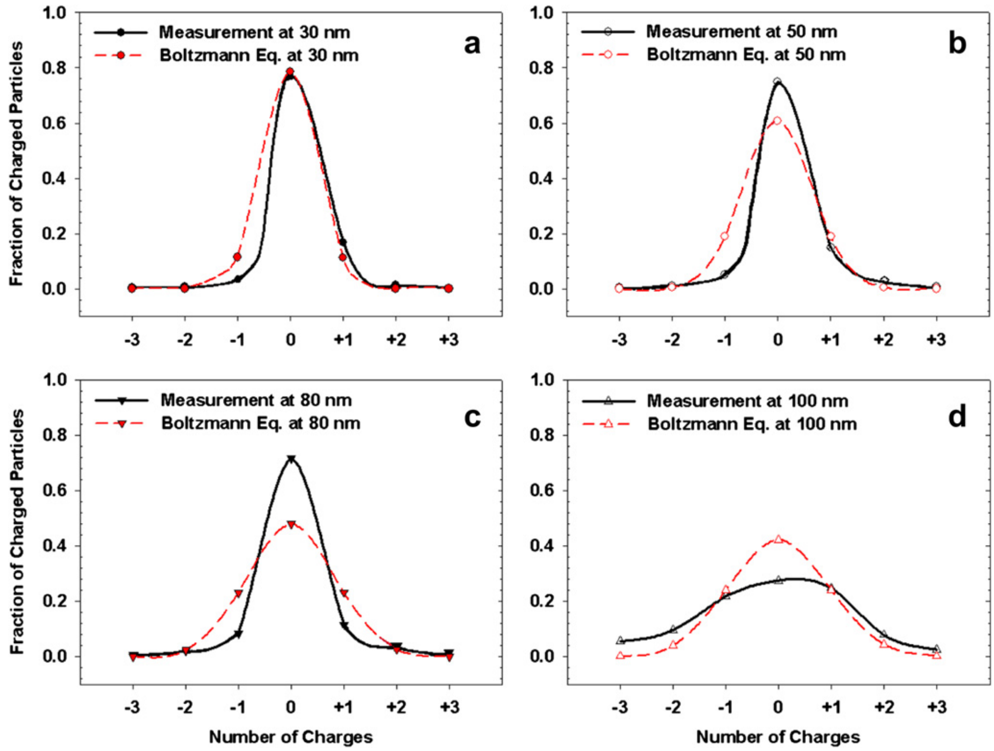

Fig. 9. Measured and Boltzmann equilibrium particle charge distributions at different electrical mobility diameters: (a) 30 nm, (b) 50 nm, (c) 80 nm, and (d) 100 nm. The filled symbols are the averages; note that the uncharged (i.e., $n = 0$) particle fractions were estimated from the measurements of charged particles by subtracting from 1. The dash-lines are the Boltzmann charge equilibrium distributions estimated at temperature of 15 °C for different electrical mobility diameters.

50 nm particles, the number concentrations were much higher for positively than for negatively charged particles (Fig. 7e, f). For larger particles (i.e., 80 and 100 nm), the magnitude of the measured concentrations was similar with minimal differences (Fig. 7c, d, g, h).

Fig. 8 presents the average fractions of particles carrying n charges with respect to different electrical mobility diameters, confirming that these particles, collected near freeways, carried net positive charges. For 30 and 50 nm particles, the total fraction of positively charged could be as high as 0.20 whereas the negatively charged fraction remained less than 0.06. Although different size particles could take different amount of positive vs. negative charges, the differences of the charged fraction with opposite signs were greatly reduced at 100 nm. Net positively charged particles and asymmetric charge distributions have been reported previously in low pressure flames (Wegert et al., 1993). Although Maricq (2008) concluded that charged particles from engine combustion processes followed Boltzmann charge equilibrium showing symmetric charge distributions, a closer examination of the published data suggested net positive charges in somewhat asymmetric distributions. The study also mentioned that steady operation of the engine was required to achieve steady-state Boltzmann equilibrium suggesting unsteady operation may result in unsteady-state charge distributions with net positive charges.

To clarify this, Fig. 9 compares data presented in Fig. 8 to Boltzmann charge equilibrium for different electrical mobility diameters. In general, for 30 nm particles, the magnitude of measured charge distribution agreed with the theoretical equilibrium, but skewed to the right, that is, with more positive charges and less negative charges (Fig. 9a). For 80 and 100 nm particles, we observed more symmetric charge distributions about zero; that is, the fraction of particles with n positive charges equal the fraction with n negative charges. However, the magnitude of measured charge distribution deviated from the Boltzmann equilibrium and the differences increased with increasing particle sizes. This is presumably because the theory assumed that particles were spherical, but larger UFPs tended to be agglomerates having more complex geometries and larger surface areas for potential ion collisions than spherical particles. In addition, the theory assumes steady-state equilibrium but due to the intermittent nature of traffic emissions at the sampling site and short distance to the source, the charged particles might not have reached their steady-state equilibrium. Consequently, nucleation mode particles have a strong tendency of carrying net positive charges at electrical mobility diameter of 30 and 50 nm. The charge distribution became rather symmetric at 80 and 100 nm but had not reached the steady-state or Boltzmann charge equilibrium in the near-freeway environment.

4. Conclusions

A series of field experiments were conducted to quantify the fractions of UFPs carrying n positive or negative charges in on- and near-freeway environments. Using a tandem DMA system, we observed that UFPs took up to three charges on and near freeways. The total fraction of charged particles ranged from 0.12 to 0.32 on the freeways in comparison with less than 0.10 in the background. The total fraction of the charged particles was on the same order of magnitude but higher on the diesel traffic dominated I-710 than the gasoline traffic dominated I-405 across the studied electrical mobility diameters.

Near freeways, the number concentration of charged particle decayed immediately within a short distance (i.e., 10 m) from the freeway and then approached to the background level at ~100 m. The decay rate for charged particles was faster than total particle number concentrations, but slower than total ion concentrations downwind from the freeway. Among charged particles, the highest decay rate was observed for particles carrying three charges. The near-freeway measurement also found nucleation mode particles (i.e., 30 and 50 nm) had a strong tendency of carrying net positive charges. For 80 and 100 nm particles, we observed more symmetric charge distributions about zero; but the charge distributions had not reached the steady-state or Boltzmann charge equilibrium near freeways.

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